

UNIVERSITY OF TECHNOLOGY SYDNEY

DOCTORAL THESIS

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# Fundamental advances in focused electron beam induced processing

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*Author:*

James BISHOP

*Supervisors:*

Professor Milos TOTH

Dr Charlene LOBO

*A thesis submitted in fulfillment of the requirements  
for the degree of Doctor of Philosophy*

*in the*

Electron beam chemistry group  
School of mathematical and physical sciences

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## Declaration of Authorship

I, James BISHOP, declare that this thesis entitled, “Fundamental advances in focused electron beam induced processing” is submitted in fulfilment of the requirements for the award of Doctorate of Philosophy in the school of Mathematical and Physical Sciences at the University of Technology Sydney. The work presented within is my own. I confirm that:

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- This research is supported by an Australian Government Research Training Program Scholarship.

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UNIVERSITY OF TECHNOLOGY SYDNEY

# *Abstract*

Faculty of Science

School of mathematical and physical sciences

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## **Fundamental advances in focused electron beam induced processing**

by James BISHOP

Focused electron beam induced processing (FEBIP) is a direct-write nanofabrication technique that utilizes the electron beam of a scanning electron microscope (SEM). It encompasses the sub-techniques of electron beam induced deposition (EBID) and electron beam induced etching (EBIE). Deposition or etching is driven by electron irradiation induced decomposition of gaseous precursor molecules adsorbed to a substrate. The nature of the precursor and substrate material determine whether deposition (EBID) or etching (EBIE) occurs. EBID enables high resolution, direct-write material deposition for fabrication of arbitrary 2D or 3D nanostructures. EBIE enables direct-write etching of select materials.

One of the key advantages of EBID is the capabilities for direct-write 3D nanofabrication. However, deposition kinetics are more complex for the fabrication of 3D nanostructures, relative to the deposition of planar (0 - 2D) structures. Previously published demonstrations of complex 3D nanofabrication using EBID, have thus far been limited to the utilization of a small parameter space, namely high electron beam energies and low beam currents. A thorough experimental and theoretical investigation of 3D EBID kinetics is performed to identify the underlying factors that make 3D EBID more complex than planar EBID. Experimental results are supplemented with simulations utilizing the Monte Carlo and finite element methods. It is concluded that electron beam induced heating, typically negligible in planar EBID, is the key factor differentiating 3D EBID kinetics from their planar counterpart. Heating is shown to occur by two mechanisms, (1) thermalization of primary electrons and (2) Joule heating. The former mechanism is active during planar EBID and only becomes significant for 3D nanostructures as a result of severely restricted heat dissipation. The latter heating mechanism is expected to be unique to 3D EBID. The effects of heating upon nanostructure morphology and means of controlling the heating are demonstrated. These results should aid in the optimization of future 3D nanofabrication with EBID.

EBIE has in general, received less research attention than EBID. Influences of multiple precursor species and orientation dependent etching in single crystal materials have not been examined. The influences of these factors is determined for EBIE

of single crystal diamond using a thorough experimental and theoretical investigation. Experiments are supplemented with density functional theory calculations. It is shown that EBIE of diamond using oxygen gives rise to rapid, isotropic etching, whilst the addition of hydrogen gives rise to crystallographically anisotropic etching and the formation of topographic surface patterns. The etch reaction pathways are determined and etch anisotropy is caused by preferential passivation of specific crystal planes by hydrogen adsorption. It is shown that the anisotropy can be controlled by the partial pressure of hydrogen and by using a remote RF plasma source to radicalize the precursor gas. It can be used to manipulate the geometries of topographic surface patterns on diamond, as well as nano- and micro-structures fabricated by EBIE. The process can be used to fabricate perfectly symmetric structures in diamond at the nano- or meso-scale and to selectively expose  $\{110\}$  and  $\{111\}$  crystal planes. The findings constitute a comprehensive explanation of anisotropic EBIE, and advance present understanding of electron-surface interactions in general.

The major limitation of EBID is the typically low material purity obtained. Thermally driven chemical vapour deposition (CVD) from the same precursors used for EBID, is generally capable of deposition of films of far higher purity and quality. In the final chapter, electron beam induced surface chemistry patterning, is used to enable selective, patterned deposition of metallic films by thermal CVD. Three surface chemistry patterning methods, all utilizing the electron beam of a SEM are examined. The efficacy of each method for restriction of thermal CVD deposition to the patterned surfaces, is evaluated for common precursors. A continuum model of selective CVD is also presented that aids the prediction of growth parameters for optimum selectivity of thermal CVD processes in general. The results pave the way towards realization of selective CVD processes, enabled by electron beam surface chemistry patterning, that may obtain the advantages of EBID, namely high spatial resolution and applicability to substrates of arbitrary composition and geometry, without the disadvantages of low material purity.

## List of peer reviewed publications

- **James Bishop**, Marco Fronzi, Christopher Elbadawi, Vikram Nikam, Joshua Pritchard, Johannes Froch, Ngoc Duong, Michael Ford, Igor Aharonovich, Charlene Lobo and Milos Toth. “Deterministic nanopatterning of diamond using electron beams”, *ACS nano*, 12 (2018), 3, 2873.
- **James Bishop**, Alan Bahm, Joshua Pritchard, Chris Elbadawi, Mehran Kianinia, Charlene J. Lobo, and Milos Toth. “Three dimensional electron beam induced deposition”, *ACS nano*, Under review.
- Aiden martin, Alan Bahm, **James Bishop**, Igor Aharonovich and Milos Toth. “Dynamic Pattern Formation in Electron-Beam-Induced Etching”. *Physical Review Letters*, 115 (2015), 25, 255501.
- **James Bishop**, Toan Trong Tran, Igor Aharonovich, Charlene Lobo and Milos Toth. “Nanofabrication using a new class of electron beam induced surface processing techniques”. *US Patent Application US20170073814A1*, 14/851,962. 2017.
- **James Bishop**, Milos Toth and Charlene Lobo. “Electron beam surface functionalization for selective chemical vapor deposition”, Submitted.
- Sejeong Kim, Johannes Froch, Joe Christian, Marcus Straw, **James Bishop**, Daniel Totonjian, Kenji Watanabe, Takashi Taniguchi, Milos Toth, and Igor Aharonovich. "Photonic Crystal Cavities from Hexagonal Boron Nitride", *Nature communications*, 9 (2018), 1, 2623.
- Christopher Elbadawi, Roger Tormo, Zai-Quan Xu, **James Bishop**, Taimur Ahmed, Sruthi Kuriakose, Sumeet Walia, Milos Toth, Igor Aharonovich and Charlene Lobo. "Encapsulation-free stabilization of few-layer black phosphorus". *ACS applied materials and interfaces*, 10 (2018), 29, 24327.
- **James Bishop**, Charlene Lobo, Aiden Martin, Mike Ford Matthew Phillips and Milos Toth. “The role of activated chemisorption in electron beam induced deposition”, *Physical review letters*, 109, 146103.
- **James Bishop**, Milos Toth, Matthew Phillips and Charlene Lobo. “Effects of oxygen on electron beam induced deposition of SiO<sub>2</sub> using physisorbed and chemisorbed tetraethoxysilane”, *Applied physics letters*, 101, 211605.





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# List of commonly used acronyms

AFM	Atomic force microscope
BSE	Back-scattered electron
CL	Cathodoluminescence
CLS	Cathodoluminescence spectroscopy
CP	Charged particle
CVD	Chemical vapor deposition
DFT	Density functional theory
DUV	Deep ultraviolet
EBID	Electron beam induced desposition
EBIE	Electron beam induced etching
EBIED	Electron beam induced etching and deposition
EBIH	Electron beam induced heating
EBL	Electron beam lithography
EBSD	Electron backscattered diffraction
ECP	Electron chaneling pattern
EDS	Energy dispersive X-ray spectroscopy
EDX	Energy dispersive X-ray spectroscopy
EL	Electron limited regime
EM	Electron microscope
ESEM	Environmental scanning elctron microscopy
ETD	Everhart Thornley detector
FEB	Focused electron beam
FEB	Focused electron beam
FEBIP	Focused electron beam induced processing
FEG	Field emission gun
FIB	Focused ion beam
FWHM	Full width at half maximum
GS	Growth surface
HT	High tension
HV	High vacuum
ITR	Interfacial thermal resistance
JH	Joule heating
KE	Kinetic energy
MC	Monte Carlo
MFC	Mass flow controller
MIL	Magnetic immersion lens
MIM	Magnetic immersion mode
MTL	Mass transport limted regime
NIL	Nano imprint lithography
NS	Non-growth surface
ODP	Oil diffusion pump
PE	Primary electron

PL	Photolithography
PLS	Photoluminescence spectroscopy
PVD	Physical vapor deposition
RT	Room temperature
SE	Secondary electron
SEM	Scanning electron microscope
SPL	Scanning probe lithography
STEM	Scanning transmission electron microscopy
TEM	Transmission electron microscopy
TEOS	Tetraethoxysilane
TMP	Turbo-molecular pump
UHV	Ultra high vacuum
VP	Variable pressure
WD	Working distance
XPS	X-ray photoelectron spectroscopy



# Physical Constants

Speed of Light	$c_0 = 2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$
Boltzmann's constant	$k_b = 8.6173303 \times 10^{-5} \text{ eV/K}$
Electronic charge	$e = 1.60217662 \times 10^{-19} \text{ C}$
Stefan Boltzmann constant	$\sigma_b = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$



# List of commonly used symbols

Parameter	Symbol	Units
Adsorbate residence time	$\tau$	s
Atomic number	$Z$	dimensionless
Backscattered electron coefficient	$\eta$	dimensionless
Concentration of adsorbed precursor molecules	$N_p$	molecules/m <sup>2</sup>
Concentration of deposited molecules	$N_D$	molecules/m <sup>2</sup>
Concentration of surface sites available for adsorption	$\Lambda_p$	dimensionless
Concentration of surface sites available for nucleation	$\Lambda_n$	dimensionless
Cross-section for electron induced dissociation	$\sigma$	m <sup>2</sup>
Density	$\rho$	kg/m <sup>3</sup>
Desorption attempt frequency	$\kappa$	s <sup>-1</sup>
Desorption energy	$E_p$	eV
Desorption rate	$k_d$	molecules/s
Diffusion coefficient	$D$	cm <sup>2</sup> /s
Diffusion path length	$l_d$	nm
EBID pillar base width	$W_b$	nm
EBID pillar height	$H_p$	nm
EBID pillar tip width	$W_t$	nm
EBID pillar width	$W_p$	nm
Energy	$E$	J
Electrical conductivity	$\sigma_c$	Sm <sup>-1</sup>
Electrical resistivity	$\rho_r$	$\Omega$ .m
Electron	$e^-$	electrons
Electron beam accelerating voltage	$V_0$	kV
Electron beam current	$I_b$	nA
Electron beam diameter	$d$	nm
Electron flux	$f$	electrons. $\mu$ m <sup>-2</sup> s <sup>-1</sup>
Electron beam half-convergence angle	$\alpha$	°
Electron interaction volume	$V_e$	$\mu$ m <sup>3</sup>
Electron optical brightness	$\beta$	Am <sup>-2</sup> sr <sup>-1</sup>
Electron optical reduced brightness	$\beta_r$	Am <sup>-2</sup> sr <sup>-1</sup>
Heat flux	$Q$	Wm <sup>-2</sup>
Mass	$m$	kg
Maximum penetration range of electrons	$R_e$	nm
Power	$P$	W
Precursor depletion	$P_d$	dimensionless
Precursor flux	$F$	molecules $\mu$ m <sup>-2</sup> s <sup>-1</sup>
Relativistically corrected beam potential	$U$	eV
Secondary electron yield	$\delta$	dimensionless
Sites per adsorbate	$n$	dimensionless
Specific heat capacity at constant pressure	$C_p$	JK <sup>-1</sup>
Sticking co-efficient	$s_p$	dimensionless

Substrate temperature	$T_s$	K
Surface coverage	$\theta$	dimensionless
Temperature	T	K
Thermal conductivity	$k$	$\text{Wm}^{-1}\text{K}^{-1}$
Time	t	s